measurably affected by the permanent gases. Heating removes the permanent gas which is adsorbed, cleaning up the surface of the oxide, and restores the surface adsorption of water vapor to its normal value.

Summary

The adsorption isotherms of water on manganese dioxide have been determined at -17.5, 0, 25 and 40°, and corresponding isotherms for benzene at 0 and 25°. The isotherms consist of two parts due to surface adsorption and condensation of the vapor on the surface of the oxide. Polanyi's theory of adsorption is in agreement with the data.

When the temperature of outgassing is raised, the surface adsorption for water is greatly reduced, due to the destruction of active adsorption patches. The treatment of the oxide with a permanent gas which can be adsorbed reduces the surface adsorption of water vapor and leaves the part of the isotherm due to condensation unaltered. The use of vapor isotherms in predicting the catalytic behavior of an oxide has been discussed.

The isotherms exhibit hysteresis and the present experiments indicate that this phenomenon is not due to false equilibrium or the presence of permanent gases on the surface of the oxide.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, UNIVERSITY COLLEGE OF SCIENCE]

MEASUREMENTS OF THE ELECTROMOTIVE FORCE OF THE CALOMEL ELECTRODE AGAINST THE HYDROGEN ELECTRODE AT LOW CONCENTRATIONS OF HYDROCHLORIC ACID

BY JNANDRANATH MUKHERJEE AND KALI KUMAR KUMAR

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Introduction

It is well known that the calomel electrode is not reliable at concentrations of hydrochloric acid below 0.03 N.[1] There is a difference of opinion as to the causes responsible for the unreliability of calomel electrodes.[2] Our observations generally corroborate previous authors and deal with the questions (a) how far the observed potential can be taken as a measure of the actual concentration of the hydrochloric acid in the cell, and (b) the nature of the chemical reactions responsible for the observed change in concentration.

Experimental

The chemicals used were Merck's "Reagent" or Kahlbaum's "pro analyse" quality purified as usual. The hydrogen was obtained from electrolysis of a strong solution of

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[1] Ellis, THIS JOURNAL, **38**, 737 (1916); Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

[2] See Clark, "Determination of Hydrogen Ions," The Williams and Wilkins Co., Baltimore, 3rd ed., **1928**, p. 309.

caustic potash. Dolezalek type hydrogen electrodes, prepared from borosilicate glass, having ground-glass joints were used. The type of calomel cell was a simplified form of that given by Clark.[3] Our measurements relate to the e. m. f. of the system $Hg-HgCl/HCl(C_1)/HCl(C_2)/HCl(C_2)/(Pt)H_2$. A set of three to four calomel electrodes was set up against a hydrogen electrode. A tall cylinder filled with acid of approximately the same concentration was interposed between the two electrode vessels. The side tubes of the electrodes dipping into the cylinder were kept plugged except when measurements were taken. The thermostat was kept at 35 ± 0.1°. A Leeds and Northrup K type potentiometer (bridge wire calibrated in the laboratory) was used. The galvanometer used was very sensitive up to 0.01 *N* hydrochloric acid but not so with more dilute solutions. The hydrogen electrode vessels after cleansing with conductivity water were rinsed several times with the solution in which the electrode was completely immersed. Hydrogen was passed into the vessel for two hours, at first keeping it at room temperature. The electrode vessel was then removed to the thermostat and the stream of hydrogen was continued for about two hours more, though one hour was found to be sufficient for attainment of equilibrium.

Calomel Electrode.—The paste was prepared by gently shaking for half an hour the hydrochloric acid solution with about 1 cc. of mercury and 5 to 8 g. of calomel powder in a 100-cc. (wide mouth) stoppered bottle. The bottle was then kept in a thermostat for about two days. Jena glass vessels were used for dilute solutions less than 0.05 *N*. The supernatant solution was then removed and titrated against standard baryta with phenol red as indicator and the change in concentration was noted. The bottle was then refilled with acid solution previously saturated with calomel and the whole procedure repeated. Both the calomel electrode vessel and the cylinder interposed between it and the hydrogen electrode were kept in the thermostat for two days before the e. m. f. was measured.

A. The Observed E. m. f. and the Concentration of the Acid.—On passing hydrogen gas for a long time, the concentration of acid increased slightly and to avoid this the e. m. f. within an hour after attainment of a steady value was noted. An appreciable fall of the concentration of the acid in the calomel electrode vessel was observed even in 0.05 *N* solution. It will be seen from Table I that the concentration was found to correspond approximately to the observed e. m. f. In the case of the more dilute solutions the change in concentration was considerable and a correction (Nernst's formula has been used) for the liquid junction potential resulting therefrom was felt necessary. The activity coefficients as generally given in the literature refer either to the freezing point or to 25°. The present measurements were made at 35° at which temperature Ellis[1] gives a value of 81.4 for 0.1 *N*. The values given by Lewis and Randall[4] have been found to disagree with the results of very careful measurements of Randall and co-workers.[4,5] For a proper extrapolation it is necessary to know the heats of dilution at different temperatures. The heat capacities[6] have been given

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[3] Ref. 2, p. 304B.

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, p. 362.

[5] Randall and Vanselow, THIS JOURNAL, **46**, 2434 (1924).

[6] Lewis and Randall, Ref. 4, p. 279.

by Randall and Ramage,[7] but the recent determinations of these quantities by Randall and Rossini have not yet been published.[8] An examination of the activity coefficients given by Randall and Young[9] shows that at 0.1 N the activity coefficients at the freezing point and at 25° are, respectively, 80.22 and 79.56, a difference of 0.66. This difference will evidently be smaller at the lower concentrations. By extrapolation the value for the activity coefficient at 25° for 0.1085 N is found to be 79.26. We have taken the value 79.0 for 35°. The existence of the liquid junction potential makes such an approximation permissible and high accuracy is not claimed. In Table I are given C_1, the concentration of the acid in the calomel vessel (as determined after the measurement of the e. m. f.); C_2, the concentration in the hydrogen electrode; the observed e. m. f. ($E_{\text{obs.}}$); E_1, the liquid junction potential calculated as above; E_x, the magnitude only of the e. m. f. which corresponds to the difference in e. m. f. at either electrode if the concentration of the acid around it had the same value as that in the other electrode and assuming that the activity coefficient is the same for the concentrations in the two electrode vessels; E_{c_1}, the e. m. f. of the cell (Pt) $H_2/HCl(C_1)/HgCl{-}Hg$ is given by $E_{\text{obs.}} - E_1 + E_x$; E_{c_2}, the e. m. f. of the cell (Pt) $H_2/HCl(C_2)/HgCl{-}Hg$ is given by $E_{\text{obs.}} - E_1 - E_x$; γ in Table II denotes the percentage activity coefficients of the acid calculated as above. The value of N_c, the transport number of hydrogen ions at 35°, has been taken to be 0.815.[10]

TABLE I

EXPERIMENTAL DATA

	c_1	c_2	$E_{\text{obs.}}$	E_1	E_x	E_{c_1}	E_{c_2}
1	0.1085	0.1085	0.3957	0	0	...	...
2	.0555	.0555	.4290	0	0	...	...
3	.0209	.02508	.4771	0.0030	0.0048	0.4789	0.4693
4	.0162	.0172	.4911	.001	.00157	.4917	.4886
5	.0112	.0126	.5085	.0019	.0031	.5097	.5035
6	.0102	.0113	.5114	Annulled (Saturated KCl	.0027	.5141	.5087
7	.00365	.00403	.5645		.0026	.5671	.5619
8	.00343	.00403	.5667		.0042	.5709	.5625

Sometimes at the lower concentrations the titer of the acid in the electrode vessel was found to have decreased by as much as 20% after the e. m. f. measurement. At the last three concentrations, instead of calculating the liquid junction potential, a saturated solution of potassium chloride was inserted. The activity coefficients given in Table II show, in view of the uncertainty as to the liquid junction potential, that the change in the concentration of the acid is mostly responsible for the observed unreliability

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[7] Randall and Ramage, THIS JOURNAL, **49**, 93 (1927).

[8] See Randall and Young, *ibid.*, p. 996, footnote (a).

[9] Ref. 8, p. 995.

[10] Landolt-Börnstein, "Tabellen," **1911**, pp. 1122, 1124.

TABLE II

CALCULATED ACTIVITY COEFFICIENTS

Concn.	0.1085	0.0555	0.02508	0.0209	0.0172	0.0162
γ (obs.)	(79)	82.5	84.7	85.7	86.6	86.7
γ (R. and Y. at 25° by interpolation)	79.26	82.4	86.4	87.3	88.1	88.4
Concn.	0.0126	0.0113	0.0102	0.00403	0.00365	0.00343
γ (obs.)	88.7	88.8	90.7	92.3	92.3	90.7 (?)
γ (R. and Y. at 25° by interpolation)	89.6	90.0	90.4	93.5	93.8	93.9

of the calomel electrode, and that the slight trace of mercuric chloride which may be assumed to be present has little effect. The influence of such factors as grain size, surface structure, or incomplete equilibrium between the different regions of the system suggested by previous workers[2] is of minor importance. The procedure used had, however, the effect of minimizing their influence.

B. The Chemical Reactions Responsible for the Observed Change in Concentrations.—The progressive diminution of the concentration of the acid in a mixture containing calomel and mercury is illustrated in Table III. On introduction of electrolytic oxygen, the rate increases markedly, while on expulsion of the dissolved oxygen the reaction practically ceases, in conformity with the experience of others.

In a 500-cc. Jena glass-stoppered bottle about 300 cc. of 0.0108 *N* hydrochloric acid solution was taken and 13.5 g. of mercury and 5 g. of mercurous chloride were added. The bottle was made air-tight with a coating of paraffin, shaken for an hour and kept in the thermostat. A measured volume of the supernatant liquid was withdrawn at different intervals and titrated against a standard solution of baryta (0.0176 *N*). The bottle was made air-tight after each withdrawal of the liquid. The decrease in acid concentration has been given as percentage of the original.

TABLE III

DIMINUTION OF ACID CONCENTRATION

Days	1	2	3	4	5	8	9	12	25
Decrease, %	1.3	6.6	7.2	12.0	20.0	22.8	25.0	41.0	58.8

On the ninth day the solution (about 200 cc.) was saturated with electrolytic oxygen, shaken and kept in the thermostat.

The possible chemical reactions[11] are: (a) the oxidizing action of the dissolved oxygen and the action of the liberated chlorine (or of hypochlorous acid formed). No evidence could be obtained of this direct oxidation with starch iodide. (b) Interaction of acid and mercury in presence of oxygen. Calomel is known to be formed from mercury and a solution of potassium

[11] See Mellor, "A Comprehensive Treatise on Inorganic Chemistry," Vol. IV.

chloride in the presence of dissolved air. We have confirmed this and reaction (b). Using 50 cc. of 0.01 *N* potassium chloride and 13 g. of mercury in a Jena glass bottle, a *P*H of 7.4 developed in eight days and simultaneously a gray deposit of calomel became visible. With 50 cc. of 0.01 *N* hydrochloric acid, a 2% decrease was observed in ninety days, but no reaction for mercuric ions with hydrogen sulfide was obtained in this case or in that of the e. m. f. measurement. The above measurements were repeated at room temperature after driving off the oxygen by boiling, followed by passage of hydrogen at room temperature and then boiling once more. No sign of formation of calomel nor any change in concentration could be observed.

(c) Mercurous chloride may react directly with oxygen. Mercurous chloride, in contact with the acid and air for a week, shows no change in the concentration of the acid. Pure oxygen, however, reacts more quickly with calomel, and mercuric ions can be detected by hydrogen sulfide.

The main reaction thus appears to be (b) above. A mixture of calomel and mercury, however, reacts more rapidly than mercury alone, possibly owing to the formation of mercuric chloride (from the oxychloride in presence of the acid), which disappears as mercurous chloride. Mercurous chloride may also have a direct effect on the velocity of the reaction.

The following experiments (Table IV) show the erratic variations of the concentration when the supernatant solutions are replenished. Four bottles of ordinary glass, each containing 13 g. of mercury, 5 g. of calomel and 50 cc. of 0.024 *N* hydrochloric acid were kept as usual in the thermostat; 25 cc. of the acid required 25.8 cc. of standard baryta. In each case, after the supernatant liquid had been withdrawn for titration, as much of it as possible was decanted without disturbing the paste and 50 cc. of the original solution was again added. The days are counted since the acid was first added to the bottle.

TABLE IV

VARIATIONS OF CONCENTRATION

Interval	4th day		7th day		10th day	
No. of bottle	Titer	% change in concn.	Titer	% change in concn.	Titer	% change in concn.
I	23.6	8.5	23.2	10.0	23.2	10.0
II	23.2	10.8	22.0	14.9	22.6	12.4
III	23.4	9.3	21.9	15.1	20.5	20.5
IV	25.0	3.0	24.7	4.2	22.0	14.8

	12th day		14th day		16th day		42d day	
No. of bottle	Titer	% change in concn.	Titer	% change in concn.	Titer	% change in concn.	Titer	% change in concn.
I	23.5	8.9	24.5	5.0	24.8	3.9	22.5	12.7
II	22.3	13.5	24.4	5.4	24.0	7.0	19.2	25.5
III	23.0	10.8	22.5	12.7	24.1	6.6	22.4	13.1
IV	24.4	5.4	24.8	3.9	24.9	3.5	20.0	22.4

Summary

To summarize, we find (a) that although presence of oxygen and mercury are both essential, mercurous chloride plays an important part in the reaction leading to the formation of calomel and loss of hydrochloric acid and (b) that the observed e. m. f. corresponds within the limits of experimental error, to the actual concentration of the acid in the electrode vessel.

92, UPPER CIRCULAR ROAD
CALCUTTA, INDIA

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF MCGILL UNIVERSITY]

HYDROGEN DISULFIDE

BY K. H. BUTLER AND O. MAASS

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Although hydrogen persulfide was discovered in 1777 by Scheele,[1] it has not proved an attractive subject for investigation and advances in the knowledge of the substance have been made slowly. Sabatier[2] succeeded in distilling the liquid in vacuo. This line of attack was followed by Block and Höhn,[3] who showed that crude hydrogen persulfide gave on fractionation two compounds, H_2S_2 and H_2S_3. Walton and Parsons[4] repeated and extended this work, using quartz apparatus in part.

In the present work the optimum conditions for the preparation of hydrogen disulfide were investigated, a method of purification was developed and the physical properties of the pure substance were determined.

Preliminary Experiments.—Preliminary experiments, which followed closely the final procedure, dealt with the effect of varying composition of the sodium polysulfide on the yields of the products. The results are given in Table I.

TABLE I

EFFECT OF COMPOSITION OF REACTANTS ON YIELD OF PRODUCTS

Polysulfide	Dilution[a]	Crude oil, g. per 100 g. total S	H_2S_3 G. per 100 g. crude oil	H_2S_2 G. per 100 g. crude oil
Na_2S_2	750	47	29.0	7.8
$Na_2S_{2.25}$	700	60	21.9	9.3
$Na_2S_{2.50}$	700	59	23.6	13.5
Na_2S_3	650	81	28.6	5.6
Na_2S_4	600	80	25.5	5.6

[a] Dilution indicates weight of solution per gram mole of sodium polysulfide.

The crude oils obtained from the different solutions varied considerably in appearance and properties. The crude persulfide from Na_2S_2 was a

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[1] "Chemische Abhandlung von der Luft und dem Feuer," p. 162.

[2] Sabatier, *Bull. soc. chim.*, [2] **44**, 169 (1885).

[3] Block and Höhn, *Ber.*, **41**, 1961 (1908).

[4] Walton and Parsons, THIS JOURNAL, **43**, 2539 (1921).